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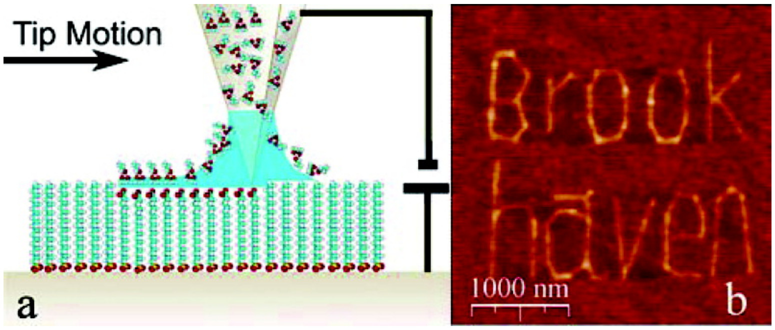

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Abstract: We introduce Electro Pen Nanolithography (EPN), a nanoscale chemical patterning technique. In a single sweep of an ink-coated, biased conducting Atomic Force Microscope (AFM) probe-tip, an underlying thin organic film is oxidized, and the ink molecules are transferred directly to the oxidized regions. Results using trialkoxysilane inks with functional terminal groups are presented, where the same ink-covered tips are used to image the pattern with zero bias. This technique provides very fast—exceeding 10 μm/s—writing speeds with line-widths as small as 50 nm. Controlled multi-write operations permit the growth of an integer number of molecular layers. Multiple chemical patterns using a single probe-tip are demonstrated.

Introduction

A chemically patterned surface is composed of regions with distinct chemical identities that may have different charge, hydrophobicity, or reactivity. Chemically patterned surfaces on the nanolength scale provide the unique opportunity to direct the assembly, orientation, structure and growth of biomolecules,[1,2] biominerals,[3] nanoparticles, and block copolymers.[4,5] As such, chemically patterned templates are relevant to many emerging nanoscale applications, including biological sensors,[6] microfluidic devices,[7] self-assembled lithographic masks,[5] and molecular electronics.[8,9] One of the most promising techniques for creating customized chemical patterns is Dip Pen Nanolithography (DPN),[10] a scanning probe technique used to transfer "ink molecules" such as thiols, silanes, or proteins from the ink-coated tip to a surface, typically gold or silicon oxide.[11−17] This method has been successfully employed to create biomolecular nanoarrays and templates for the self-assembly of nanoparticles.[1,15−17] Here we demonstrate a new chemical patterning technique, Electro Pen Nanolithography, where molecules are selectively transferred and anchored to a surface in the desired pattern. This technique opens a range of new possibilities for customizing two-dimensional and three-dimensional chemically functionalized nanopatterns on surfaces with a variety of different surface chemistries.

Experiments

Octadecyltrichlorosilane (OTS), bicyclohexyl (BCH), and toluene (99.8%) were purchased from Sigma-Aldrich, and mercaptopropyltrimethoxysilane (MPTMS) was obtained from Gelest, Inc. The Si(100) wafers (Unimore Inc., Resistivity 0.5−10 Ohm·cm) were cleaned in piranha solutions at 125 °C for 10 min and subsequently rinsed with distilled water. The OTS self-assembled monolayer films were prepared by dipping the cleaned silicon wafers in a fresh 5 mM OTS bicyclohexyl solution for 8 h and then rinsed with toluene while ultrasonicating for 1 min. The conducting AFM tips (titanium−platinum coated, CSC-17, MikroMarsch) were prepared by UV cleaning followed by dipping them into the ink solution for 30 min. For the MPTMS ink, concentrations ranging from 1:100 to 1:400 (v/v) MPTMS:toluene solutions were used to coat the tips. During the AFM patterning, the OTS-coated wafer was positively biased, and the conducting AFM tip was connected to the "virtual ground" of the current pre-amplifier. The pattern fabrication was carried out using a Molecular Imaging PicoPlus AFM operating in contact mode with a typical contact force of 1−10 nN and with a positive sample bias voltage of 5−10 V relative to the tip. A humid environment with a controlled relative humidity (RH) close to 100% was typically used. The patterns were characterized using the same AFM, either in situ with the same ink-coated tips used for patterning in contact mode or ex situ with clean tips in either tapping or contact mode. Although similar images were obtained using both modes, the coated tip imaging required less setup. All images are unfiltered.

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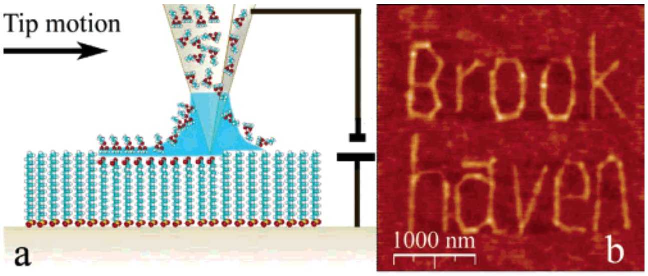

Figure 1. Molecular scale schematic of Electro Pen Nanolithography along with a typical pattern prepared with this technique. (a) Schematic of the Electro Pen Nanolithography writing process on an OTS-coated surface. The terminal methyl group of the OTS is converted to a reactive COOH-terminated surface (OTS_{ox}) by applying a voltage between the conducting AFM tip and the conducting silicon substrate in a humid environment. "Ink" molecules are delivered from the "inked tip" to the reactive OTS_{ox} surface, thus forming a second layer in the same sweep. No second layer is formed on the methyl-terminated regions. (b) A typical EPN pattern demonstrates the ability to write 50 nm wide lines with the MPTMS ink. The darker background regions are the OTS film.

Results and Discussion

Figure 1 illustrates the EPN method and shows an AFM image of an EPN-prepared pattern. The EPN method transfers molecules to the surface using probe-tips inked with the desired molecule, as with Dip Pen Nanolithography (DPN), but also involves an electrochemical reaction directly under the probe tip. Here we demonstrate the method using a doped silicon substrate coated by a ~2.6 nm thick self-assembled monolayer of octadecyltrichlorosilane (OTS), a molecule with a methyl-terminated, 18 carbon alkyl chain. A patterned surface prepared with EPN, imaged with the same ink-covered tip at 0.0 V bias, is shown in Figure 1b. This image demonstrates 50 nm wide lines that are about 0.7 nm high, the height of a single molecular layer.

Whereas EPN utilizes the same electrooxidation nanoreaction used in Constructive Nanolithography,[18−20] only EPN provides the direct delivery of ink. This electrooxidation nanoreaction, developed by Sagiv and co-workers, electrochemically converts the terminal methyl group of an OTS-coated silicon surface to a hydrophilic, carboxylic acid-terminated (OTS_{ox}) terminated surface by a voltage-biased conducting AFM tip. In the Constructive Nanolithography[18−20] process, additional molecular layers are deposited ex situ by dipping the OTS_{ox} patterned surface in a solvent containing the desired molecules, and these molecules are preferentially adsorbed on the oxidized regions. With EPN, a monolayer of ink molecules is formed in *a single-step* writing process that first oxidizes the underlying OTS layer to OTS_{ox} and then transfers the ink from the tip to the higher surface energy OTS_{ox} regions in situ. This fast one-step process offers several advantages over Constructive Lithography, including in situ multi-write capabilities and real-time monitoring of the pattern formation (see below). The EPN ink transfer process is similar to DPN, developed by Mirkin and co-workers,[10] except that the surface under the tip is first prepared to adsorb the ink through the electrooxidation process. With DPN, the line width depends on the diffusion speed of the ink and follows a dependence that scales as the square root of the writing speed. In contrast, with EPN, the line width is ultimately controlled by the width of the underlying OTS_{ox} lines, and these lines may be as narrow as 25 nm.[18,19] The important role of humidity in all of the conducting probe-tip nanolithographies strongly suggests that a capillary "water bridge" (see Figure 1a) forms between the tip and the surface.

In separate control experiments, we fabricated the same pattern under the identical conditions described above, except that the tip was not coated with ink. The patterns fabricated appeared 0.3−1 nm lower than the surrounding OTS layers, similar to what Sagiv and co-workers observed.[18−20] These patterned regions are carboxylic acid-terminated hydrocarbon chains, "OTS_{ox}". Alternatively, under drier conditions ($<$30% RH) and significantly slower writing speed (typically $<$0.25 μm/s), the underlying silicon is oxidized and raised features are observed.[21−24] Through this control experiment, we conclude that, under our writing parameters, silicon oxide is not formed and thus the raised patterns after the EPN writing are not composed of silicon oxide or ink monolayer formed on silicon oxide in the absence of OTS_{ox}.

We have successfully employed two classes of "inks": the trialkoxysilane and quaternary ammonium salts. The image shown in Figure 1b was created using a tip coated with MPTMS using a 9 V bias and a patterning speed of 5 μm/s. The letters written are clearly visible where the feature height is ~0.7 nm high. With EPN, the bias voltage influences the pattern line width and writing speed.[25]

To demonstrate the chemical nature of the pattern, a different MPTMS pattern, see Figure 2a, was produced with intentionally wide lines (~300 nm). A typical cross-section shows that the second layer is 0.7 ± 0.1 nm above the OTS surface, a thickness very close to the expected 0.7 nm height of the extended, standing-up ink molecule.[12,26] Figure 2c shows the same region of the surface after 2 nm diameter maleimide mercapto cross-linker-modified gold nanoparticles were chemically attached to the patterned surface from a 1:1 2-propanol:water solution containing the nanoparticles.[27] The AFM image shows that the nanoparticles were preferentially located above the patterned regions. As illustrated in Figure 2d, the height of the patterned regions increased by about 2 nm after exposing the surface to the maleimide mercapto cross-linker-modified gold nanoparticles. To ascertain that the nanoparticles were chemically bonded to the MPTMS, experiments were carried out in contact mode with sufficient force (50−100 nN) to move molecules and particles laterally, so-called "tip plowing". The results of these high-force experiments, carried out with a MikroMarsch NSC-14 tip (5 N/m force constant), showed that the nanoparticles could not be removed independently from the MPTMS. Measurements carried out at low applied force did not remove either the MPTMS or the nanoparticles, whereas measurements at high applied force (50−100 nN) removed both the nanoparticles and MPTMS but not the OTS_{ox}. Together, these results indicate that the nanoparticles are not physisorbed on the

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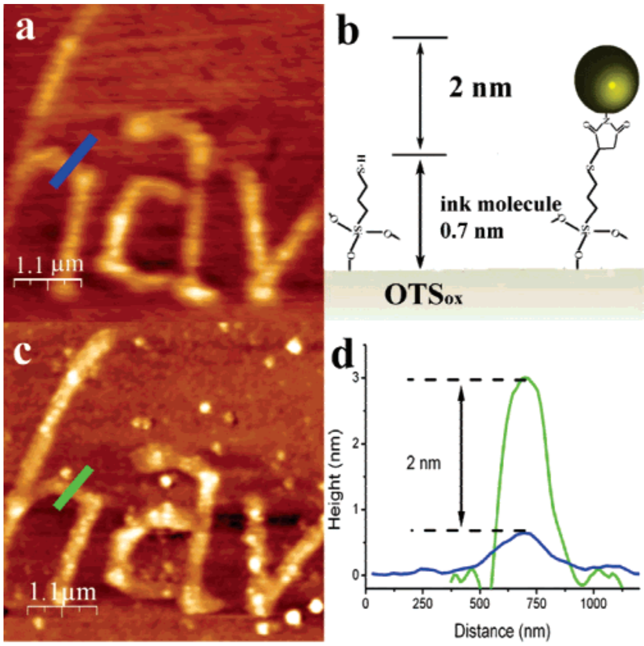

Figure 2. AFM images of an Electro Pen Nanolithography pattern written using MPTMS ink. (a) A typical EPN pattern (5.8 × 5.8 μm^2 image) written on the OTS surface with 9 V at 5 μm/s speed. The height of the pattern is measured to be 0.7 ± 0.1 nm. (b) Proposed molecular structure of MPTMS on the OTS_{ox} surface (left) and after gold nanoparticles, coated with a single maleimide mercapto linker, is adsorbed (right). The overall particle size is about 2 nm. For graphical purposes, the ink molecular scale was expanded. (c) After reacting the EPN writing pattern with the coated nanoparticles. The nanoparticles selectively bond to the SH-terminated MPTMS regions. The bright dots are much larger clusters, which are physisorbed on the OTS. The images were obtained in tapping mode, with a MikroMarsch NSC-15 tip. (d) Height profiles of the pattern before and after the gold nanoparticles were introduced. The blue and green profiles correspond to the respective green and blue paths shown in (a) and (c). The blue line demonstrates the 0.7 nm thickness of the MPTMS molecule, and the green curve demonstrates the additional 2 nm thickness of the nanoparticle, as expected.

MPTMS patterned regions; rather, they must be directly bonded to the MPTMS molecules. Since the mercapto group tends to be slowly oxidized to disulfide in air, it is possible that a small fraction of the surface mercapto groups were oxidized to disulfide during the course of our measurements. However, the AFM measurements are unable to resolve the difference between mercapto and disulfide groups, which have similar chemical behaviors. Considering the short sample exposure time in air (<1 h) and the strong affinity of the nanoparticles to the MPTMS regions, we conclude that the regions patterned with MPTMS must be mainly SH terminated. We also note that the MPTMS pattern survives adhesive tape peeling and extended immersion in ethanol, toluene, acetone, and chloroform.

The trialkoxysilanes were selected as inks due to their relatively slow reactivity with water, especially when compared to that of trichlorosilane molecules (including OTS), which are so reactive that they instantaneously polymerize in the humid environment. For the alkoxylsilanes, it is well-known that the silane hydrolysis reaction can be catalyzed either by an acidic or basic environment.[28] With the EPN writing process, the acidic OTS_{ox} surface (see Figure 1) appears to provide the required environment to catalyze the hydrolysis, thus promoting the formation of the self-assembly of a second layer. The second layer is anchored to the carboxylic acid-terminated OTS_{ox} surface either by hydrogen bonds or by ester bonds. The acidic environment should also promote lateral cross-linking between the molecules to form a two-dimensional polymer network, in addition to the anchoring to the underlying layer. A unique aspect of EPN is that multilayer patterns can be generated. Figure 3 illustrates overlapping lines written with MPTMS ink. Although there are small variations in the height of a single line, on average, they are 0.7 nm high. The intersection of two lines (see B) is about 1.5 nm high, and the intersection of three lines (see C) is about 2.2 nm high. Thus, the height profile at any position appears to vary linearly with the number of lines drawn with the slope equal to the length of the molecule. In the absence of an applied potential, the film thickness does not increase with the number of scans. Further, we note that the raised features cannot be ascribed to an underlying silicon oxide, as discussed in the control experiments above. Together, these results suggest that multilayer EPN patterning with MPTMS relies on an oxidation mechanism. This oxidation mechanism is either an oxygen radical-based reaction, suggested by J. Sagiv and co-workers,[18,25] or an anodization reaction that converts the terminal SH group of the MPTMS to SO_3^{2-}/SO_4^{2-} groups.[29,30] The anodization reaction usually occurs at lower voltage (1−5 V), while the oxygen radicals' oxidation occurs at higher voltage (>5 V).[29,30] Both reactions appear to be plausible under our writing conditions (∼10 V), and we do not have data to distinguish between the two. For both mechanisms, the final product is the same SO_3^{2-}/SO_4^{2-} terminated surface. The acidic surface is also hydrophilic, and like the carboxylic acid surface, it acts to catalyze the trimethoxysilane hydrolysis and cross-linking. Similarly, the third layer grows on the top of the second layer. Such stepwise growth of patterns has potential for building multilayer, three-dimensional, nanolandscapes and may have potential applications in multibit information storage.

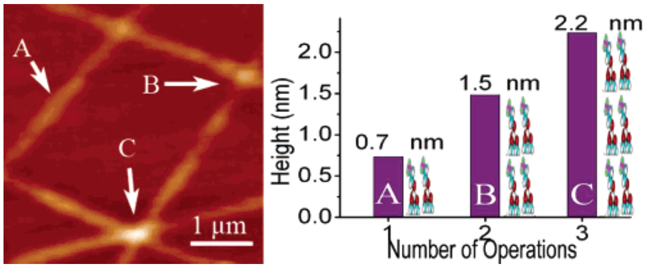

Figure 3. Electro Pen Nanolithography multilayer writing capabilities are demonstrated using MPTMS ink. (a) An EPN pattern consisting of overlapping MPTMS lines, ∼200 nm wide, on a 4.2 × 4.2 μm^2 image field prepared using a 10 V bias. The single line at A is 0.7 ± 0.1 nm high, the two line crossing point at B is 1.5 ± 0.1 nm high, and the three line crossing point at C is 2.2 ± 0.1 nm high at their highest points, respectively. (b) Bar graph of the heights obtained from points A, B, and C from (a). The stepwise growth demonstrates the ability to create 3D landscapes with EPN.

The proposed EPN writing mechanism is based on an extensive understanding—developed by others and in our laboratory[18,25]—of the electrochemical oxidation process of the terminal methyl group of OTS to a terminal acid group. The essential finding is that the OTS monolayer is converted to OTS_{ox} through an oxidative reaction involving atomic oxygen or oxygen radicals that are generated in the water electrolysis

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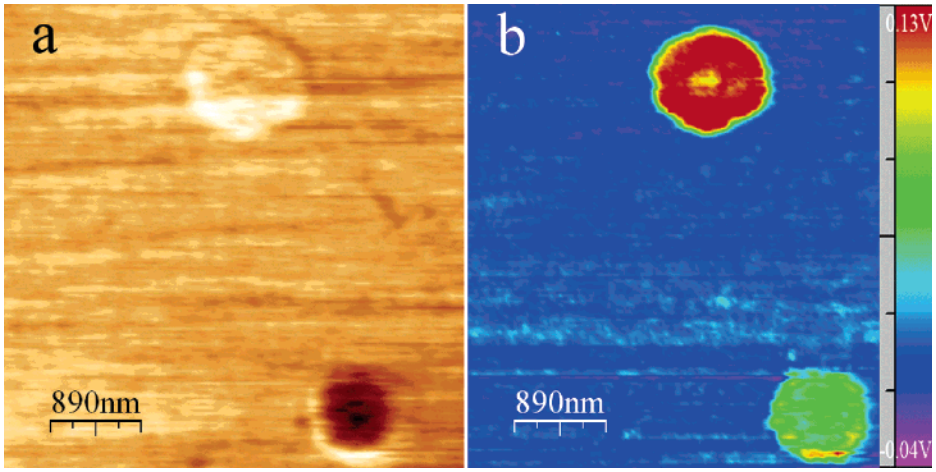

Figure 4. EPN multichemical patterning demonstrated with a “marginally inked” MPTMS ink using a single inked tip. These patterns were prepared using a tip prepared with a dilute, 1:400 (v/v) MPTMS:toluene solution. The two dots were created with a 9 V pulse at a stationary position for ~1 s. The upper dot was rastered for 20 min to deposit the MPTMS ink. The lower dot was not rastered after the potential pulse. The topography image (a) and friction image (b) show the different height and chemical natures of the pattern. The upper dot is SH-terminated, while the lower dot is COOH-terminated.

reaction that occurs between the tip and OTS substrate. Although these radicals are produced directly under the tip, where the electric field is the highest, they can diffuse laterally through the water and oxidize unreacted OTS at the boundary between the OTS_{ox} and OTS regions. This lateral diffusion/reaction process continues until either the applied voltage is removed or the water bridge is broken.

The formation of a single molecularly thick line at all writing speeds and conditions instead of a multilayer structure provides an important clue into the nature of the EPN ink delivery process. The ink molecules coated on the AFM probe are physisorbed, and they will coat the air−water interface upon the establishment of a tip−substrate water bridge forming a Langmuir film. The ink molecules must be transferred to the OTS_{ox} surface via the air−water interface of the water bridge and not directly through the interior of the water bridge since the ink molecules are not water soluble. If the ink were to be deposited directly under the tip inside the water bridge, then multilayers would form at a stationary tip position or during a single sweep. Thus, the ink molecules are only transferred to the surface via the air−water interface of the water bridge after the tip has been translated laterally. The essential elements of the proposed writing mechanism are illustrated in Figure 1a.

According to the mechanism presented, the EPN resolution and patterning speed should be limited by the OTS_{ox} line-widths of the Constructive Lithography writing process in which 25 nm wide lines—several times the tip radius—have been achieved by others[18,19,25] and our group. The line width increases with increasing humidity, temperature, bias voltage, and decreasing writing speed.[25] Line widths of 50 nm have been achieved with MPTMS ink using a patterning speed of 10 μm/s, the fastest speed of our AFM instrument. Further studies are required to ascertain the ultimate resolution of this technique.

To terminate patterning with DPN, it is necessary to break contact with the surface, whereas with EPN, writing is stopped by setting the bias to 0 V, thus maintaining the water bridge. In principle, this should be a faster and a more reliable process. The ability to turn off the writing with potential control also allows repeated imaging with the ink-coated tip at very slow speeds for many hours, a feature not possible with DPN.

The ink delivery speed from tip to the OTS_{ox} pattern is affected by the ink concentration. To demonstrate this, we fabricated EPN patterns with MPTMS ink that were only imaged with a clean inkless (nonconducting) tip in tapping mode rather than using the inked tips with zero bias. These images were very similar to those obtained with the inked imaging tips, and this indicates that the ink (applied to the tip with a 1:400 (v/v) MPTMS:toluene solution) is delivered during a single writing process. For tips coated with a lower ink concentration, slower ink delivery (incomplete ink coverage on the OTS_{ox} patterns) was observed, and only after repeated scanning/imaging were fully covered MPTMS patterns obtained. We have also used these marginally inked tips to create two very different chemical patterns using the same tip. Figure 4 shows topographic (a) and friction (b) mode images of two dots (700−800 nm diameter) fabricated on the OTS surface using a marginally inked MPTMS inked tip. Both dots were prepared by exposing the OTS surface to a 9 V bias for ~1 s at a fixed tip position. For the lower dot, there was insufficient ink to coat the COOH-terminated surface with ink in the writing process. For the upper dot, the tip was rastered over the COOH-terminated dot at 0 V for 20 min in order to deposit sufficient ink to coat the dot with MPTMS. In topographical mode, the top dot reveals a height of 0.73 nm, consistent with a monolayer of MTMPS. The different chemical surface species are apparent from the friction mode images (Figure 4b). It should also be possible to generate an additional chemical pattern with the same “marginally inked” tip by electrooxidizing the terminal SH. Ink molecules with multiple oxidation states may hold the possibility of creating potential dependent chemical patterns.

In addition to using MPTMS as the ink, we have also fabricated EPN patterns with 3-aminopropyltrimethoxysilane and octadecyltrimethoxysilane (not shown). There is a wide variety of commercially available trialkoxysilanes with different terminal functionality since these molecules are extensively used as industrial cross-linkers and surface modifiers. Most of these can be used as inks. In addition to trialkoxysilane inks, we have also created EPN patterns using quaternary ammonium salts as the ink. In this case, since the carboxylic acid-terminated OTS_{ox} surface is partially negatively charged, the ink molecules are anchored to the OTS_{ox} surface by ionic forces. The patterns

(<100 nm in width) written by this type of ink are stable in organic solutions, and they can be removed in aqueous ionic solutions. By combining these two features, it is possible to use the quaternary ammonium salts as a protective layer in the first processing step while allowing these regions to be exposed after removing the ink in the second step.

Electro Pen Nanolithography is a new method for the direct writing of molecules on surfaces into robust molecular layers. This high-speed writing technique is capable of both monolayer and stepwise, three-dimensional surface patterning. Structural characterization can be readily carried out in situ using the same inked tip with zero applied potential. The variable chemical patterning functionalities available make this an ideal tool for fabricating nanoscale chemical patterns on surfaces, and these might be applied to a variety of different nanoscale applications.[5−9] EPN is a complementary method to DPN and extends ink-based nanolithography to surfaces coated with thin organic films. Many new developments in DPN, such as ink well and multi-probe cantilever, could also be incorporated into EPN. In the future, extensions to EPN may allow for the direct writing of biological patterns.

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